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Immobilization of Hg (II) to Hg (0) on Reducing Dehydrated Carbons

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***Abstract*—Hg (II) is one of the most toxic elements in the aquatic environment and its immobilization as water insoluble form of Hg (0) is the aim of this research. Dilute sulfuric and phosphoric acids were used to prepare sulfuric acid dehydrated carbon (SDC) and phosphoric acid dehydrated carbon (PDC), respectively from peanut shell at 170 ^{o}C. Removal of Hg (II) from aqueous nitrate solution was tested at different initial pH, contact time, concentration and temperature. Maximum sorption took place at initial pH 2 and equilibrium obtained within ~ 70 hr on both carbons with increased uptake as temperature rises. Activation energy, E_a, was >40 kJ/mol indicating chemical adsorption. Hg (II) uptake was found to follow well the Langmuir adsorption model with higher uptake for SDC than PDC. Temperature rise led to increased removal of Hg (II) on both carbons. Scanning electron microscopy (SEM) showed micro-droplets of Hg (0) on the carbon surface that was confirmed using energy dispersive spectroscopy (EDS). Hg (II) reduction was accompanied by surface oxidation. Hg (0) was collected from mercury loaded carbons via sonication under water. Dehydrated carbons shows promising results for Hg (II) immobilization as Hg (0).**

***Index Terms*—dehydrated, carbon, Hg (II), reduction, sulfuric, phosphoric**

I. INTRODUCTION

Mercury is very toxic in addition of being non-essential element. Its presence in the environment poses a potential threat to human health even at very low concentrations. It can cause brain damage, dysfunction of liver, gastrointestinal tract, kidney, and central nervous system [1]. Hg (II) is the most prevalent form of mercury in aquatic ecosystems, however, its biochemical conversion into a more toxic form (methylmercury) by microorganisms is kinetically feasible both in water and soil [2]. Thus, it is necessary that mercury is removed from wastewater before its transport and discharge into the environment. Based on WHO standards [3], the maximum contaminant level for mercury in wastewater is 0.001 mg/L. Major sources of mercury in wastewater are effluents from chlor-alkali, metallurgical processes, paper and pulp, oil refining, electrical, rubber processing and fertilizer industries [2]. Traditional methods for the removal of heavy metals from water include hydrometallurgical technologies, ion exchange, electrodialysis, reverse osmosis, precipitation and adsorption. Different sorbents have been used for the removal of mercury from aqueous solutions including peat [4], lignite [5] peanut shell carbon [6] and flax shive dehydrated carbon [7]. Peanut shell (hull) is an agricultural waste that is produced worldwide in considerable quantities every year with partial use in animal feed formulations or for energy [8]. In this paper, peanut shell was transformed to dehydrated carbons using dilute sulfuric and phosphoric acids. Dehydrated carbons are tested for the removal and reduction of Hg (II) from aqueous nitrate solutions.

II. EXPERIMENTAL

A. Sorbent Preparation

Peanut shell was received from a local company and was cut to small pieces (<1 cm length) followed by distilled water washing to remove dirt, dust and other impurities. The shell was left to dry in open air at room temperature. The sorbent was prepared as follows: Clean air-dried peanut shell (20 g) was mixed with 200 mL of 2 M sulfuric or phosphoric acid and the mixture was heated to 170 ±1 ^{o}C in an oven for 12 hrs. The resulting black material was allowed to cool, and then washed in a Buchner funnel under vacuum until the wash water did not show a change of methyl orange color. The carbonized wet product (acid free) was dried in an oven at 120 ^{o}C to constant weight, transferred to a desiccator to cool and finally stored in a dry, clean and well-closed polyethylene jar. The carbons were ground and a size range between two sieves of 16 and 60 mesh selected for the sorption experiments.

B. Hg (II) Sorption

All the chemicals used were of analytical grade. A stock solution of 1500 mg/L of Hg(II), was prepared in distilled water using mercury (II) nitrate, $Hg(NO_3)_2$. All the working solutions were prepared by diluting the stock solution in distilled water. In the kinetic experiments, samples of 0.1 g of the dry carbons were mixed with 200 mL of Hg (II) (100 mg/L) at initial pH 3 at different temperature (25-45 ^{o}C). Initial pH 3 was selected, as shown later, for Hg (II) sorption in the kinetic and equilibrium experiments to avoid possible precipitation especially at higher Hg (II) concentrations. At different periods of time, aliquot of supernatant was withdrawn for metal analysis.

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The effect of pH on metal sorption was studied for Hg (II) concentration (200 mg/L) at different pH values (pH 1.5–5.0). The pH was adjusted by adding few drops of 0.1 M nitric acid or 0.1 M sodium hydroxide before the addition of the pre-weighed sorbent. The pH values of solutions before and after sorption were recorded. Batch experiments were carried out by mixing 50 mL of metal solution of desired concentration, pH and temperature, with 0.06 g of the carbon for Hg (II) sorption in a shaking water bath (100 rpm) until equilibrium was reached. The isotherm studies were carried out at initial pH 3 for Hg (II) concentration range of 100-1250 mg/L, at different temperature (25-45 °C). After the equilibrium was reached, aliquot of supernatant was withdrawn and metal concentration was analyzed. Samples of wastewater (50 mL) spiked with Hg (II) (300 mg/L) were tested for Hg (II) sorption at pH 3.0 using 0.06 g of both carbons.

C. Hg (II) Analysis

Total Hg was analyzed using Hydride-generation atomic absorption spectroscopy (AAS). The analysis was performed using a SpectraAA 220FS operating in the flame mode. Liquid samples containing Hg were added to the Hg vapor-generation flask along with 10 mL of 0.5 M hydrochloric acid (HCl). Sodium borohydride ($NaBH_4$) was used as a reducing agent to generate elemental Hg in a solution of 5% $NaBH_4$ and 1% potassium hydroxide (KOH) w/v [9]. Experiments and analysis have been carried out three times and maximum analytical error was found to be less than 5%.

D. Characterization of SDC and PDC

Cation exchange capacity (CEC) was measured using a standard method [10]. Base neutralization capacity was measured by Boehm titrations [11]. Surface zero point of charge (pH_{zpc}) was also analyzed following the procedure of Moreno-Castilla *et al.* [12]. Surface area was also investigated using via nitrogen adsorption at 77 *K* (Quantachrome Instruments, USA).

The sorbent surface, before and after the reaction with Hg (II) solution, was examined for scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). SEM pictures were taken using a Scanning Electron Microscope (Jeol, Japan) at an accelerating voltage of 20 kV. The scanning electron microscope was equipped with an EDS system (Jeol, Japan). The instrument focuses electrons at certain locations on the sorbent surface in order to displace electrons in the orbital shells of the trace elements. A discrete quantity of energy is given out as electrons fall back into vacant orbitals, thereby, revealing the identity of the elements present. X-ray powder diffraction was conducted using a Philips PW 1830 generator with a Philips PW 1050 powder goniometer (Philips, USA). Copper K_α was used as the incident radiation. Infrared spectra were obtained using FT-IR spectrometer (Spectrun BX, Berkin Elmer, Germany) for SDC and PDC after drying at 120 °C for 2 hours. 0.01 g of each sample was mixed with ~ 1 g of KBr and the mixture was pressed into a pellet at high pressure. The pellet was scanned in transmission mode through a wavelength range from 4000 to 600 cm^{-1} with background subtraction.

III. RESULTS AND DISCUSSION

A. Physicochemical Characterization of SDC and PDC

X-ray diffraction patterns of both carbons showed that the structure of both carbons is amorphous (figure not shown). The infrared spectra of both carbons are presented in Fig. 1. The broad band in the range of 3400-3450 cm^{-1} in both carbons is related to the (O-H) stretching vibrations. The OH groups are associated by means of hydrogen bonds as the frequency of free OH groups is sharp and located above 3500 cm^{-1}. The bands at 2914 cm^{-1} and 2843 cm^{-1} for DC denote the presence of stretching C-H vibrations in CH_3 and CH_2 groups. The bands at ~1624-1630 cm^{-1} for both carbons is related to the stretching vibrations of carbonyl containing functional groups, stretching vibrations of COO-, and/or skeletal C=C vibrations. The bands in the range of 1380–1000 cm^{-1} are assigned to the C−O stretching and O−H bending vibrations such as phenols and carboxylic acids.

SDC surface is more acidic than PDC surface as SDC possesses lower pH_{zpc} and higher CEC than PDC reflecting the presence of high content of carbon oxygen groups such as –COOH on SDC than on PDC (Table I). Surface functionality from Boehm titrations showed that SDC possesses higher carboxylic, lactonic and phenolic groups than AC as presented in Table I. EDS analysis showed less carbon content and higher oxygen content for SDC than PDC reflecting the high content of carbon-oxygen groups on SDC surface (Table I). Carbonization to produce SDC and PDC can be explained as follows. By mixing the peanut shell with ~ 2 M sulfuric acid or phosphoric acid and heating at 170 °C, an extent of hydrolysis to hemicelluloses takes place with swelling of the precursor material. As the water evaporates, the acid concentrates carbonizing the plant material via the removal of water from the carbohydrate material (cellulose and hemicellulose) and causing partial oxidation to the carbonized materials. In addition partial fragmentation took place to lignin [13]. Because sulfuric acid is more powerful oxidizing agent than phosphoric acid, SDC possess more surface functional groups than PDC. This is reflected on the higher surface functionality, lower pH_{zpc}, higher oxygen and lower carbon contents of SDC than that of DPC (Table 1). The surface area of SDC is higher than that of PDC, this could be due to the harsher conditions of preparation of SDC as sulfuric acid is more powerful in its dehydration and oxidation than phosphoric acid [14]. This probably has led to wider pores of SDC. Similar low surface areas were reported earlier for dehydrated carbons prepared via sulfuric acid dehydration (from flax shive (19 m^2/g) [13] and date palm leaflets (24 m^2/g) [15]. Phosphoric acid dehydrated carbon (from date palm leaflets) possesses low surface area of 7.8 m^2/g [16]. In general, dehydrated carbon possesses much lower surface area than activated carbon as a result of the high surface functionality of the former [13], [16].

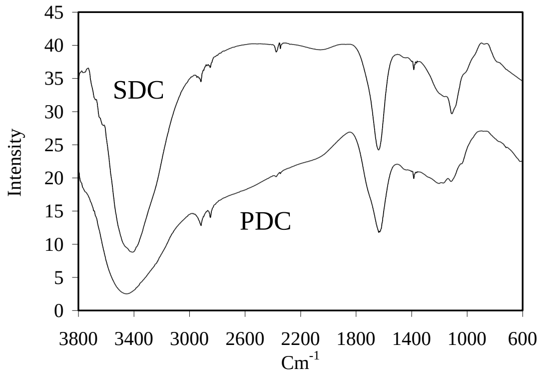

Figure 1. FTIR spectra of SDC and PDC

TABLE I. CHARACTERIZATION OF SDC AND PDC

Surface properties	SDC	PDC
pH_{zpc}	3.07	3.75
CEC (meq/g)	1.74	1.05
Surface groups		
Carboxyl (meq/g)	2.30	1.53
Lactone (meq/g)	1.50	1.34
Phenol (meg/g)	1.53	1.22
EDS analysis		
C (%)	60.7	65.8
O (%)	33.4	30.7
S (%)	1.05	0.14
P (%)	0.00	1.12
Surface area (BET) m^2/g	27.7	7.2

B. Effect of pH on Hg(II) sorption

Sorption of Hg (II) ions was low at low pH values (<3) and increases as pH increases with insignificant change in Hg (II) adsorption in the range of pH 3-5, (Fig. 2). Higher initial pH values were avoided to prevent possible precipitation. Hg (II) sorption was accompanied by a decrease in the final pH indicating protons release in solution suggesting the presence of ion exchange processes. Previous studies showed similar results of an increased Hg (II) uptake with the increase in the initial pH of sorption solution using different sorbents [7]. The aqueous Hg (II) ion hydrolyzes very readily in dilute solutions. Using 120 mg/L of Hg(II), in nitrate media, Sarkar *et al.* [17] found that at pH values < 3, Hg^{2+} is the predominant aqueous species and as the solution pH increases, the percentage of Hg(II) as $Hg(OH)^+$ and $Hg(OH)_2$ species increases.

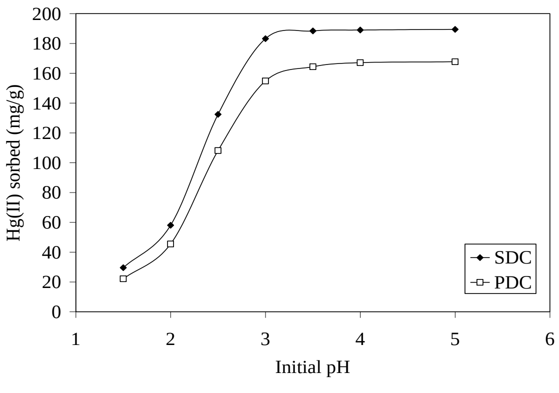

Figure 2. Effect of initial pH on Hg (II) sorption

In the present work, initial pH 3 was selected for the kinetic and equilibrium experiments.

C. Kinetics of Hg (II) Sorption

Sorption of Hg (II) that was conducted at initial pH 3 appears to be relatively slow reaching approximate equilibrium within ~ 70 hours. Pseudo second order kinetic model (Eq. 1) [18] was tested for the kinetic data.

$$t/q_t = 1/kq_e^2 + t/q_e \qquad (1)$$

where, k (g/mg/hr) are the rate constant, q_e and q_t are the amount of Hg(II) sorbed at equilibrium and at time t per unit weight of the sorbent (mg/g) respectively. The initial sorption rate $h = k_2q_e^2$ (mg/g/hr). The linear plots of t/q_t versus t showed a good fitting with high R^2 values (Table II). This indicates that the sorption of Hg (II) complies very well with pseudo second order kinetic reaction which agreed with chemisorption as the rate-limiting mechanism through sharing or exchange of electrons between sorbent and sorbate [18]. Both of k and h are slightly higher for the SDC than for the DPC (Table I) and this could be because of wider pores expected due to the harsher preparation conditions using sulfuric acid.

TABLE II. KINETIC PARAMETERS OF HG (II) SORPTION

Carbon	Temp. °C	Pseudo second order model			
		K (g/mg/ h)	h (mg/g/h)	q_e (mg/g)	R^2
SDC	25	0.000443	18.44	204	0.9997
	35	0.000898	37.91	207	0.9993
	45	0.00163	73.35	212	0.9998
PDC	25	0.00039	12.47	179	0.9992
	35	0.00080	26.13	181	0.9994
	45	0.00120	48.67	188	0.9999

A large increase in k and h was observed with temperature rise (Table II). By rising the temperature from 25 to 45 °C, k and h showed an increase to 3.7 and 4.0 folds for SDC and 3.1 and 3.9 for PDC, respectively. This could be due to an expected swelling of the dehydrated carbons with temperature rise [7], [15], [16]. The activation energy, E_a, was calculated using Arrhenius equation (Eq. 2).

$$k = Ae^{-Ea/RT} \qquad (2)$$

k refers to the pseudo second order rate constant (g/mg/hr), A is the pre-exponential factor (frequency factor), R is the gas constant (8.314 J/mol K) and T is the solution temperature (K). From the linear relationships between the logarithm of rate constants and the reciprocal of the Kelvin temperature, E_a values were found to be 51.4 and 49.5 kJ/mol for SDC and PDC, respectively, indicating that the rate-limiting process was evidently a chemical process. Low E_a (5–40 kJ/mol) values are characteristic for physisorption, while higher E_a values (40–800 kJ/mol) refer to chemisorption [19].

D. Equilibrium Sorption of Hg (II)

Sorption of Hg (II) on SDC and PDC follows an “L-type” adsorption isotherm, with increased uptake as temperature increases, Fig. 4. The experimental isotherm data showed a good fitting for the Langmuir equation, Eq. (3), (Table III).

$$C_e/q_e = 1/(b.q) + C_e/q \quad (3)$$

TABLE III. LANGMUIR CONSTANTS FOR HG (II) SORPTION

Carbon	Temp °C	Langmuir constants		R^2
		q (mg/g)	b (L /mg)	
SDC	25°C	646.0	0.0405	0.9997
	35°C	723.6	0.1202	0.9996
	45°C	817.0	0.3049	0.9993
PDC	25°C	510.2	0.0284	0.9996
	35°C	561.8	0.0846	0.9998
	45°C	613.5	0.2114	0.9995

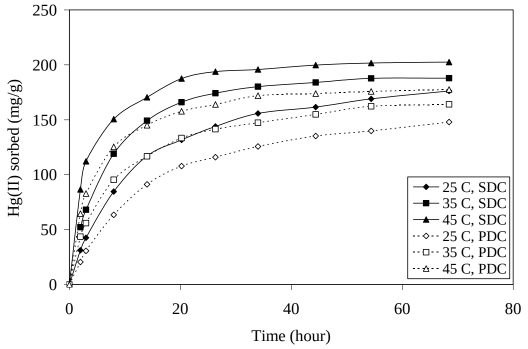

Figure 3. Kinetics of Hg (II) sorption at different temperature.

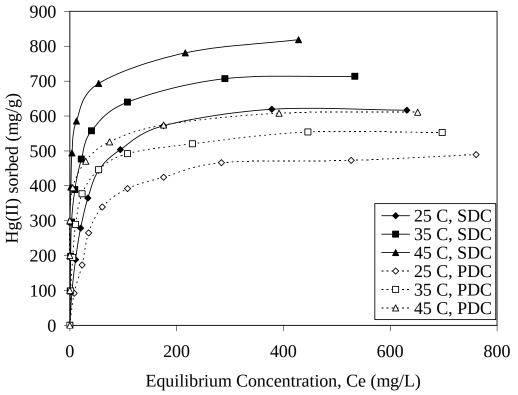

Figure 4. Sorption isotherms of Hg (II) on SDC and PDC at different temperatures.

C_e, equilibrium Hg (II) concentration; *q*, and *b* are the Langmuir constants related to maximum adsorption capacity (mg/g), and the relative energy of adsorption (L/mg), respectively. The monolayer capacity, *q* (mg/g), was slightly higher for SDC than for PDC (Table III). This could be because sulfuric acid dehydrates and oxidizes produced carbon more than phosphoric acid as the former is more powerful dehydrating and oxidizing agents than the latter [14]. As the temperature increases, sorption increases. This could be due to expected swelling of the dehydrated carbon and a consequent increase in sorption sites as found earlier for the sorption of different metal ions on dehydrated sorbents from agricultural waste [7], [15]. Peanut shell activated carbon and granular activated carbon showed capacities of 110 and 124 mg/g of Hg (II) removal, respectively [6]. Such values are obviously lower than that of SDC or PDC in this study. In another study, Flax shive dehydrated carbon using 12 M sulfuric acid showed uptake of 385 mg/g of Hg (II) and Hg (II) was immobilized as Hg (0) on its surface [7].

E. Sorption from Hg (II) Spiked Wastewater

Wastewater (50 mL samples) spiked with 300 mg/L of Hg (II) (from nitrate media) at 25 °C were tested for adsorption on both carbons at initial pH 3. Hg (II) uptake for both carbons has decreased to ~ 63 % of that obtained using deionized water. This is related to the presence of levels of Ca(II) (112 mg/L), Mg(II) (137 mg/L) and Na(I) (175 mg/L) and other trace heavy metals that compete with Hg(II) for sorption sites on both carbons.

F. SEM and EDS of Loaded Carbons

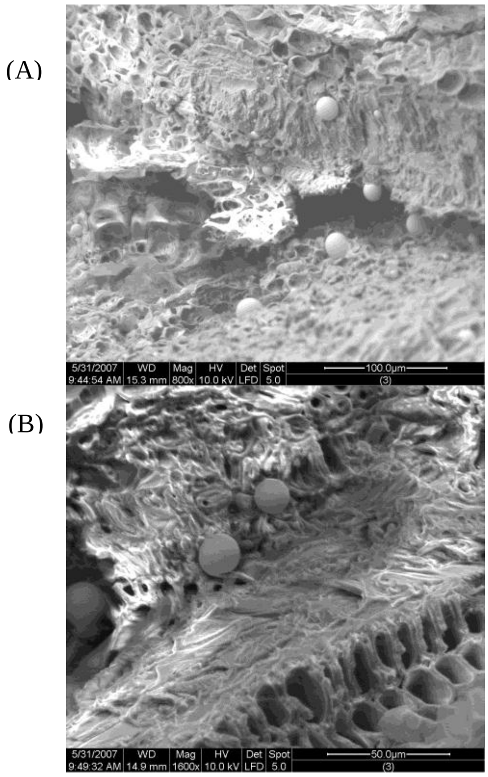

Figure 5. SEM of (A) SDC and (B) PDC loaded with elemental Hg (0).

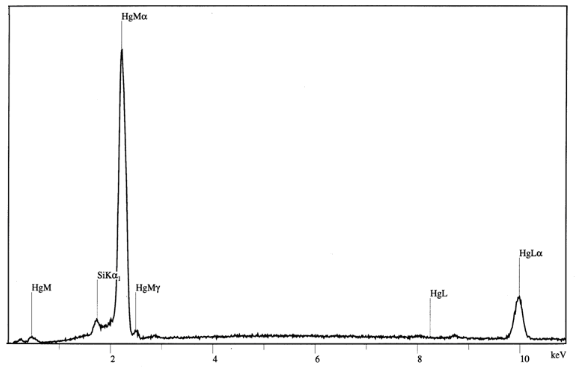

Figure 6. Typical EDS spectra of Hg droplets on both carbons

SDC and PDC samples, after reaching equilibrium with 1500 mg/L of Hg(II) at initial pH 3 and 45 °C, were separated, left to dry at room temperature and then used for SEM and EDS analysis. Mercury micro-droplets on the sorbent surface are clearly identified on SEM photographs (Fig 5). The elemental mercury micro-droplets were confirmed as elemental mercury as shown in the EDS analysis (Fig 6). This indicates that a reduction process of Hg(II) to elemental mercury took place on the sorbent surface. In a previous study, dehydrated carbon reduced $HgCl_2$ solution to the insoluble Hg_2Cl_2 crystals on the surface of a carbonaceous sorbent [7].

G. Recovery of Hg and Carbon Reuse

Loaded carbon with elemental Hg was grinded and mixed with demonized water after which it was allowed to vibrate under sonication for 15 minutes. The micro-droplets separated from the carbon particles and agglomerated by density in the bottom of the vessel. The carbon after being separated was washed by 0.5 M HNO_3 and denioized water and then dried at 120 °C. The carbons were tested for CEC, pH_{zpc} and Hg (II) loading. CEC has increased to 2.25 and 1.45 meq/g for SDC and PDC respectively. pH_{zpc} was lowered to 2.85 and 3.15 for SDC and PDC respectively. For the capacity of Hg (II) removal at 25 °C, it was lowered to ~ 161 and 107 mg/g or 25 and 21% of its maximum capacity for SDC and PDC, respectively in the first cycle.

H. Hg (II) Sorption Mechanism

The increase in CEC and the decrease in pH_{zpc} reflects an increased surface functionality after the reaction with Hg (II) ions reflecting surface oxidation. The decrease in Hg (II) uptake after the first cycle, reflects that a great extent of the reduction sites were consumed in Hg (II) reduction in the first sorption cycle. Reduction potentials of Hg (II) are presented in equations 4-6.

$$Hg^{2+} + 2e = Hg^{0} \qquad E^{0} = +0.851\ V \tag{4}$$

$$Hg^{2+} + 2e = Hg_{2}^{2+} \qquad E^{0} = +0.905\ V \tag{5}$$

$$Hg_{2}^{2+} + 2e = 2Hg^{0} \qquad E^{0} = +0.796\ V \tag{6}$$

The mechanism can be summarized as follows. Hg (II) ions are sorbed via ion exchange first and then is reduced to Hg (0) that agglomerate to form micro-droplets on the carbon surface. The reduction property is related to the presence of active reduction centers that are capable of reducing Hg (II) to Hg (0) via the donation of electrons to Hg (II) [7]. Hg (0) is being utilized in alloys and amalgams and some other instruments.

IV. CONCLUSION

Converting the water soluble, Hg (II), to the insoluble Hg (0) that can be easily separated from the aqueous media on dehydrated carbon is attractive. Dehydrated carbons is cheap, sustainable and powerful reducing sorbernt for Hg (II) ions.

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